Questions on QEq implemented in Lammps

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What is this presentation about ?

Here I shortly resume my understanding of the QEq implementation in Lammps.

In addition I write my questions on what I do not understand, so to be hopefully helpful to others.

I refer to the case qeq/slater since I am interested in that.

Quick Resume of Theory

Theory of the Algorithm - 01

The electrostatic energy is given by:

$$E_{es} = E_0 + \sum_i q_i \cdot \chi_i + \frac{1}{2} \cdot \sum_{ij} q_i \cdot q_j \cdot V_{ij} \tag{14.1}$$

The electrostatic interaction is given by:

$$V_{ij} = \int d^3 r_i \int d^3 r_j \cdot \frac{\rho_i(r_i, q_i) \cdot \rho_j(r_j, q_j)}{r_{ij}} \tag{14.2}$$

The atomic charge density distribution in a generic point of space is assumed as slater 1s orbital:

$$\rho_i(r, q_i) = Z_i \cdot \delta(r - r_i) + (q_i - Z_i) \cdot f_i(r - r_i) \tag{14.3}$$

The function f is expressed as:

$$f_i(|r - r_i|) = \frac{\xi_i^3}{\pi} \cdot e^{-2 \cdot \xi_i \cdot |r - r_i|} \tag{14.4}$$

Theory of the Algorithm

With these, the terms in eqn.(14.1) become:

$chizj[i]$

$$
\begin{aligned}
E_0 &= \text{(neglected since included into the non-electrostatic pair)} \\
\chi_i &= \chi_i^0 + \boxed{\sum_j Z_j \cdot ([j|f_i] - [f_i|f_j])} \Longrightarrow \text{(just short range)} \\
V_{ij} &= J_i^0 \cdot \delta_{ij} + [f_i|f_j] \\
[f_i|f_j] &= \left[\frac{erfc}{r} + (...)\right]_{short-range} + \frac{erf}{r}_{long-range}
\end{aligned}
$$

(...) = (Expression in zei zej)

Theory of the Algorithm

The minimum of eqn.(14.1) will be reached under the condition of $\sum_i q_i = 0$ when:

$$\begin{aligned}
\sum_j V_{ij} \cdot q_j &= \mu - \chi_i \\
q_i &= \sum_j V_{ij}^{-1} \cdot (\mu - \chi_j) \\
\mu &= \frac{\sum_{ij} V_{ij}^{-1} \cdot \chi_j}{\sum_{ij} V_{ij}^{-1}}
\end{aligned}$$

The system in eqn.(14.11) is solved in two subsystems:

$$\begin{aligned}
\sum_j V_{ij} \cdot s &= -b_s = -\chi_i \\
\sum_j V_{ij} \cdot t &= -b_t = -1
\end{aligned}$$

They are solved in Lammps one after the other.
s and t are fictitious charges. The final charge is given by:

$$q_i = s_i - \mu \cdot t_i = s_i - \frac{\sum_i s_i}{\sum_i t_i} \cdot t_i$$

Theory of the Algorithm

To make the code faster a pre-conditionig can be done on Vij by considering only the its short-ranged part:

$$V_{ij} = V_{ij-s} + V_{ij-l} \tag{14.17}$$

$$V_{ij-s} = J_i^0 \cdot \delta_{ij} \tag{14.18}$$

$$V_{ij-l} = [f_i|f_j] \tag{14.19}$$

$$V_{ij\text{-s}}^{-1} = \mathrm{Hdia\_inv}[\mathrm{i}] = 1/J_i^0 = 1/\mathrm{eta}[\mathrm{itype}]$$

Questions

Question - 01

H in lammps = Vij here

The complete H from theory would be $V_{ij} = J_i^0 \cdot \delta_{ij} + [f_i|f_j]$

Inclusive of both short and long-ranged

The short-ranged terms of the matrix H is computed in the subroutine calculate_H:

```
etmp1 = 1.00 * (ci_jfi - ci_fifj);
etmp2 = 0.50 * (ci_fifj + erfcr*rinv);

zjtmp += qqrd2e * zj * etmp1;
if (DS_debug) printf("\n-fix_qeq_slater.cpp :: -----------------------
return qqrd2e * etmp2;
```

$$H.val[m_{fill}] = kc \cdot \frac{1}{2} \cdot \left([fi|fj]_{lazic} - \frac{1}{r} + \frac{erfc}{r} \right)$$

Why is this factor ½ here ?
It is not present in the equation …

Question - 02

These seem just the short-ranged terms of the electrostatic potential.

Where are the long-ranged terms (in reciprocal space?) computed ?

I couldn't find them …

$$[f_i|f_j] = \left[\frac{erfc}{r} + (\ldots)\right]_{short-range} + \frac{erf}{r}_{long-range}$$

$\boxed{(\ldots) = (\text{Expression in zei zej})}$

Question - 03

In the function sparse_matvec, the matrix H is multiplied by x and the result stored in q.
The final expression is:

$$
\begin{aligned}
q[i] &= \left[J_i - 2 \cdot kc \cdot \left(\frac{1}{2} \cdot \frac{erfc}{r} + \frac{1}{\sigma \cdot \sqrt{\pi}}\right)\right] \cdot x[i] + \\
&+ \sum_j kc \cdot \frac{1}{2} \cdot \left([fi|fj]_{lazic} - \frac{1}{r} + \frac{erfc}{r}\right) \cdot x[j]
\end{aligned}
$$

«self» part of the long-range interactions

Factor ½ of Question-01

(This comes from the variable woself)
Where does this term come from ?
Why does the erfc appears twice in this expression ?
Where is the long-ranged (reciprocal space) term here ?

Question - 04

In the file fix_qeq_slater.cpp is also a function called calculate_H_wolf

But in the examples online this is not invoked.

What is that for ?
In what case is it invoked ?

Thank you
for your help